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Novel aqueous-phase hydrogenation reaction of the key biorefinery platform chemical levulinic acid into γ-valerolactone employing highly active, selective and stable water-soluble ruthenium catalysts modified with nitrogen-containing ligands

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ABSTRACT

High catalytic activities (TOF = 3000 h^{-1}) have been achieved by novel water-soluble ruthenium catalysts modified with nitrogen-containing ligands such as the bathophenanthrolinedisulfonic acid disodium salt (BPhDS) in the hydrogenation reaction of the renewable polar platform chemical levulinic acid (LA) which possesses a central relevance in the development of biorefineries of the future in a sustainable way to produce with essentially quantitative selectivity of 99.9 mol% γ-valerolactone (GVL) in aqueous media. The apparent activation energy of the Ru/BPhDS catalyst was calculated and amounts a relative low value of 53.3 kJ/mol when one considers that in the LA hydrogenation reaction this catalyst reduces a less reactive keto group into alcohol functionality. A recycling experiment of the Ru/BPhDS catalyst by extraction after addition of diethyl ether has shown that the catalyst is stable without loss of activity and selectivity in a consecutive run.

1. Introduction

Nowadays, carbohydrates and their derivatives from renewable biomass are considered to be the new challenge in the development of Green/Sustainable Chemistry because they possess a high potential as industrial feedstocks for biorefineries to produce biofuels, bio-based chemicals, energy/power, food, pharmaceuticals and materials and because they contribute to an effective management of greenhouse gas emissions [1–22]. The nature's biomass production capacity is huge, namely $200 \cdot 10^9$ t/a compared to only $7 \cdot 10^9$ t/a of all extracted fossil fuels [23]. The high potential of carbohydrates and their derivatives as industrial biorefinery feedstocks is even more remarkable when one considers that biomass consists to 75% of carbohydrates and only 7% of total biomass production capacity per annum is used for food, feed and non-food applications [7,23]. According to the EU Directive 2009/28/EC on the promotion of the use of energy from renewable resources by the year 2020 biofuels shall be 10% of the transportation fuels. Moreover, the EU has set such goals that the production capacity of bio-based chemicals should be 30% of the capacity of chemicals by the year 2025 [24]. The US Department of Energy (DOE) published in 2004 a report which highlighted 12 key building block chemicals so-called platform chemicals that can be obtained from carbohydrates and could be further converted to a number of high-value bio-based chemicals, materials and fuels as well [3]. In 2010, an updated evaluation revisited and extended this original list of DOE where, inter alia, ethanol and furan molecules such as furfural and 5-hydroxymethylfurfural (HMF) were also selected [4]. Levulinic acid (LA, Scheme 1) was included in both the original and extended list of DOE because it is considered as one of the most important platform chemicals of central relevance in a biorefinery for many potential industrial applications and is readily available with a low cost, simple and relatively high yield production from both C_6 and C_5 carbohydrates [4,6,8,21,25–28].

LA can be hydrogenated to γ-valerolactone (GVL, Scheme 1) which is a very attractive C_5 platform chemical and a key intermediate compound for many and different applications such as production, inter alia, of advanced biofuels e.g. valeric biofuels [2,8–10,15,16,29–34,48], bio-based fine chemicals [25,29,30,35–37,48] and polymers [25,29,30,35,48] possessing also a potential as additive for gasoline [8,29–31,36,37] and suitable for use as a sustainable polar aprotic solvent [8,29,30,36–38,48,62] as well as

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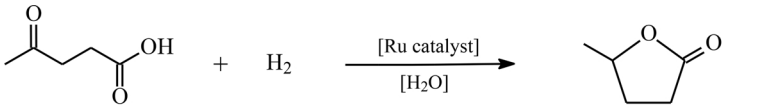


Levulinic acid (LA) γ-Valerolactone (GVL)

Scheme 1. Selectivehydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) catalyzed by water-soluble ruthenium catalysts modified with nitrogen-containing ligands in aqueous media.

a food additive [8,29,31,36]. During the last decade, the hydrogenation of LA to GVL has received considerable attention and a broad spectrum of different types of active and selective catalytic systems have been developed employing various transition metal heterogeneous catalysts in the liquid or gas phase [2,7–9,16,28,30–35,39–45], catalytic nanoparticles [46–50] and conventional homogeneous transition metal catalytic complexes [51–68].

Aqueous-phase catalysis by water-soluble transition metal complexes especially in aqueous/organic two-phase systems possesses an enormous interest because this mode of heterogenization of homogeneous catalysis combines several advantages such as: (i) high activities and selectivities under mild reaction conditions by tailoring of the coordination sphere of the metal, (ii) easy and quantitative recovery of the catalyst in active form from organic reaction products by simple phase separation, and (iii) the nature of the aqueous solvent which is a green solvent [69–75]. Water-soluble rhodium catalytic complexes modified with the sodium salt of trisulfonated triphenylphosphine [TPPTS, $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$, Fig.1] have found important industrial applications such as in the Ruhrchemie/Rhône-Poulenc process for the hydroformylation of e.g. propene in aqueous/organic two-phase systems [69,70]. The highly polar nature of the aqueous solvent makes it an ideal medium to carry out conversions of hydrophilic carbohydrates and their derivatives employing water-soluble transition metal catalytic complexes in aqueous media [76].

A pioneer work on the aqueous-phase catalytic hydrogenation of LA using water-soluble Ru/TPPMS complexes was carried out by Joó et al. [77] in 1977. The group of Horváth [78,79] applied water-soluble Ru $(acac)_3$/TPPTS catalysts in the aqueous-phase hydrogenation of LA at 140 °C within 12 h to yield 95% GVL which was isolated after extraction by addition of ethyl acetate. The group of Heeres [80] combined aqueous-phase dehydration with hydrogenation of C_6carbohydrates such as glucose and fructose using water-soluble $RuCl_3{\cdot}3H_2O$/TPPTS catalysts to yield 23% GVL. The same group [81,82] further described the biphasic hydrogenation of LA to GVL catalyzed by water-soluble $RuCl_3{\cdot}3H_2O$/TPPTS systems in a dichloromethane/water (volume ratio = 100/25) two-phase system which allows recovery and recycling of the catalyst. Tukacs et al. [83] reported the hydrogenation of LA in the absence of solvents catalyzed by $Ru(acac)_3$ modified with various sulfonated phenylalkylphosphines and found that the system Ru $(acac)_3/n\text{BuP}(C_6H_4\text{-}m\text{-}SO_3Na)_2$ exhibited a high catalytic activity of 3540 TOFs per hour to yield 99.9% GVL. Delhomme et al. [84] investigated the aqueous-phase hydrogenation of LA catalyzed by $RuCl_3{\cdot}3H_2O$ or $Ru(acac)_3$modified with water-soluble phosphine ligands such as TPPTS, monosulfonated triphenylphosphine [TPPMS, $PPh_2(C_6H_4\text{-}m\text{-}SO_3Na)$], PTA (Fig. 1) and the sodium salt of trisulfonated tris(2,4-dimethylphenyl)phosphine to achieve a maximum catalytic activity of TOF = 210 h^{-1} and selectivity towards GVL of 97%. The group of Fu [85,86] reported the hydrogenation of LA to GVL catalyzed by water-soluble pentamethylcyclopentadienyliridium(III) complexes using a range of 2,2´-bipyridine derivatives as ligands to achieve up to 12,200 TOFs per hour in aqueous media. The group of Bhanage [87] reported the aqueous-phase hydrogenation of LA to GVL catalyzed by ruthenium(0) nanoparticles created from $RuCl_3{\cdot}3H_2O$ precursors stabilized by PEG400 and found a catalytic activity of TOF = 40 h^{-1} with 99% selectivity towards GVL.

During our continuous interest in the field of aqueous-phase catalytic conversions of renewable carbohydrates and their derivatives employing water-soluble transition metal catalytic complexes one of us carried out selective carbonylation reactions of HMF catalyzed by Pd/TPPTS complexes [69,70,88–91] and applied Ru/TPPTS catalysts in an one pot approach of the hydrolysis of inulin polysaccharides combined with hydrogenation reaction of obtained fructose units towards mannitol [92] in aqueous media. We now report the efficient aqueous-phase hydrogenation of LA into GVL employing highly active, selective and stable water-soluble ruthenium catalysts modified with various nitrogen-containing ligands and the recovery of such catalysts in active form from reaction products by extraction and a simple phase separation of the biphasic system created after addition of diethyl ether without any loss of the catalytic activity and selectivity. To our knowledge, this is the first example of a hydrogenation reaction of LA into GVL using water-soluble ruthenium catalysts modified with nitrogen-containing ligands in aqueous media.

2. Experimental

2.1. Materials

Hydrogen (quality 5.0) was purchased from Air Liquide Hellas A.E.B.A. (Athens) and used without further purification. Demineralized water was deoxygenated in an ultrasound bath under high vacuum for 2 h. During the deoxygenation the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this procedure was repeated several times. Levulinic acid (LA) with a purity of 98% was purchased from Alfa Aesar and used without any further purification. γ-valerolactone (GVL) and valeric acid (VA) were obtained from Alfa Aesar. 1,4-pentanediol (1,4-PDO) and N,*N*-dimethylformamide (DMF) were purchased from Aldrich. $RuCl_3{\cdot}3H_2O$, $Ru(NO)(OAc)_3$, $Ru(NO)(NO_3)_3$, $Ru(acac)_3$, $[Ru(NO)]_2(SO_4)_3$ and $RuO_2{\cdot}H_2O$ were purchased from Alfa Aesar. TPPTS was prepared according to literature procedures [93–100] and isolated with purity higher than 98%. Tris(2-pyridyl)phosphine (T_2PyP) was prepared according to the procedure of the group of Wilkinson [101] with a purity higher than 99%. All other nitrogen-containing ligands (Fig. 1) were purchased from Acros Organics, Alfa Aesar, Sigma and Aldrich and wereusedwithoutanyfurtherpurification. NaI, NaCl, $BaCl_2{\cdot}2H_2O$ and $(CH_3CH_2)_4NBF_4$ were purchased from Alfa Aesar; $AlCl_3{\cdot}6H_2O$ was obtained from Sigma Aldrich and $NaH_2PO_4{\cdot}H_2O$ was purchased from Merck.

2.2. Procedure of a typical catalytic hydrogenation experiment

First, the autoclave was thoroughly cleaned and followed by numerous series of treatment of the autoclave at elevated temperatures (140 °C) and pressures (50 bar of H_2) within 1 h each time using an aqueous solution of BPhDS (Fig. 1) in the absence of any transition metals in order to be sure that no memory effects of the autoclave regarding previous transition metal catalytic systems are still operative. After this procedure, the hydrogenation reactions of LA were carried out in the presence of water-soluble ruthenium catalysts modified with phosphines and nitrogen-containing ligands in aqueous monophasic systems. The catalytic hydrogenation experiment of LA of entry 4/3 of Table 4 was carried out with the following procedure. The water-soluble $RuCl_3{\cdot}3H_2O$/BPhDS catalyst precursor was first synthesized by dissolving under stirring of 1.31 mg (0.005 mmol) $RuCl_3{\cdot}3H_2O$ and 2.86 mg (0.005 mmol) BPhDS (molar ratio BPhDS/Ru = 1) under argon in 5 ml deaerated demineralized water within 5 min of time. After

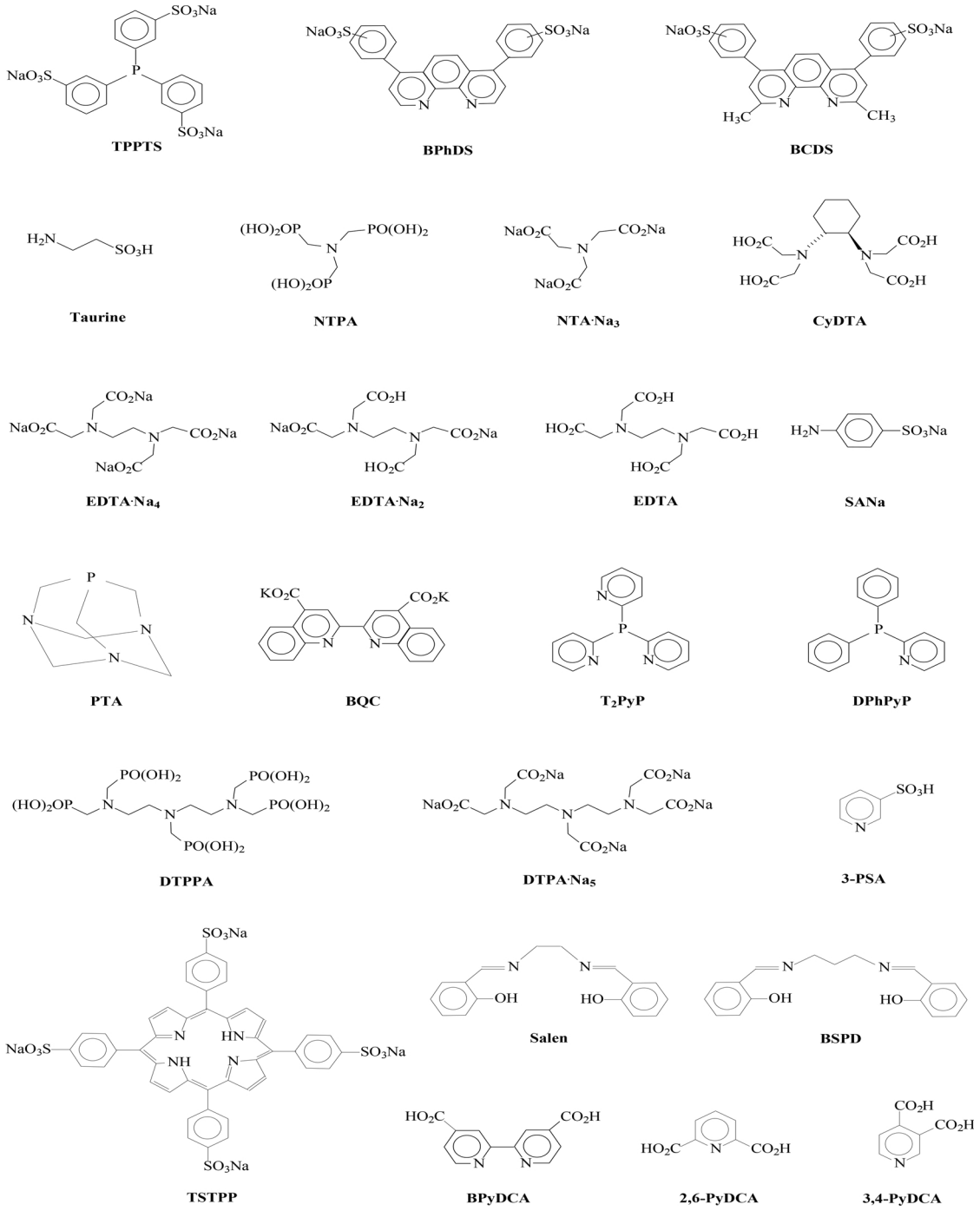


Fig. 1. Structures of the water-soluble ligands triphenylphosphinetrisulfonic acid trisodium salt (TPPTS), bathophenanthrolinedisulfonic acid disodium salt (BPhDS), bathocuproinedisulfonic acid disodium salt (BCDS), 2-aminoethanesulfonic acid (Taurine), nitrilotris(methylphosphonic acid) (NTPA), nitrilotriacetic acid trisodium salt (NTA·Na_3), trans-1,2-diaminocyclohexane-*N,N,*N´,N´-tetraacetic acid (CyDTA), ethylenediaminetetraacetic acid tetrasodium salt (EDTA·Na_4), ethylenediaminetetraacetic acid disodium salt (EDTA·Na_2), ethylenediaminetetraacetic acid (EDTA), sulfanilic acid sodium salt (SANa), 1,3,5-triaza-7-phosphaadamantane (PTA), 2,2´-biquinoline-4,4´dicarboxylic acid dipotassium salt (BQC), tris(2-pyridyl)phosphine (T_2PyP), diphenyl(2-pyridyl)phosphine (DPhPyP), diethylenetriaminepentakis(methylphosphonic acid) (DTPPA), diethylenetriaminepentaacetic acid pentasodium salt (DTPA·Na_5), 3-pyridinesulfonic acid (3-PSA), tetrasodium meso-tetra(sulfonatophenyl)porphine (TSTPP), N,N´-bis(salicylidene)ethylenediamine (Salen), N,N´-bis(salicylidene)-1,3-propanediamine (BSPD), 2,2´-bipyridine-4,4´-dicarboxylic acid (BPyDCA), 2,6-pyridinedicarboxylic acid (2,6-PyDCA), 3,4-pyridinedicarboxylic acid (3,4-PyDCA).

addition of 1.742 g (15 mmol) LA to the aqueous catalyst solution under stirring for further 5 min the reaction mixture, having a ruthenium concentration of 75 ppm, was charged into an *Autoclave Engineers* autoclave of a nominal volume of 100 ml which was previously evacuated and filled with argon. In the reaction mixture the molar ratio of LA/Ru was 3000. After a number of pressurising-depressurising cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured and contents were heated with stirring using a stir bar driven by an IKA magnetic stirrer (poorer mixing) because its own MagneDrive III agitator system was out of order (stirring rate = 700 rpm). The heating time to reach a reaction temperature of 140 °C was 5 min. At the reaction temperature of 140 °C the hydrogen partial pressure was 80 bar and the reaction time 1 h. After the reaction the autoclave was cooled (within 3 min) to room temperature, vented of hydrogen and the

Table 1
Effect of the molar ratio of ligand to ruthenium, reaction time, temperature and the nature of the water-soluble ligand on the ruthenium-catalyzed hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) in completely aqueous medium[a].

Entry	Catalyst precursor	L/Ru molar ratio	t (h)	T (°C)	Conversion LA (mol %)	Selectivity GVL 1,4-PDO (mol %) (mol %)		TOF[b] (h^{-1})
1/1[c]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	1	120	52	100	–	390
1/2[c]	$RuCl_3{\cdot}3H_2O$/BPhDS	2	1	120	42	100	–	310
1/3[c,d]	$RuCl_3{\cdot}3H_2O$/BPhDS	3	1	120	31	99.6	0.4	230
1/4[c]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	2	120	57	100	–	215
1/5[c]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	4	120	86	99.5	0.5	160
1/6[c]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	6	120	100	99.6	0.4	125
1/7[d]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	1	100	10	99.0	1.0	120
1/8[d]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	1	110	15	99.3	0.7	180
1/9[d]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	1	120	38.5	99.7	0.3	460
1/10[d]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	1	130	42	99.8	0.2	500
1/11[d]	$RuCl_3{\cdot}3H_2O$/BPhDS	1	1	140	76.0	99.3	0.7	910
1/12	$RuCl_3{\cdot}3H_2O$/BPhDS	1	1	150	83	98.7	1.3	1000
1/13	$RuCl_3{\cdot}3H_2O$ /BPhDS	1	1	160	100	99.2	0.8	1200
1/14	$RuCl_3{\cdot}3H_2O$/Taurine	2	1	140	98.5	98.8	1.2	1170
1/15	$RuCl_3{\cdot}3H_2O$/CyDTA	1	1	140	97	99.6	0.4	1160
1/16	$RuCl_3{\cdot}3H_2O/T_2PyP$	1	1	140	96	99.8	0.2	1160
1/17	$RuCl_3{\cdot}3H_2O$/BQC	1	1	140	93	99.9	0.1	1120
1/18	$RuCl_3{\cdot}3H_2O$/3-PSA	2	1	140	92	98.6	1.4	1110
1/19	$RuCl_3{\cdot}3H_2O/EDTANa_4{\cdot}4H_2O$	1	1	140	91	99.0	1.0	1090
1/20	$RuCl_3{\cdot}3H_2O$/2,6-PyDCA	2	1	140	89	99.1	0.9	1070
1/21	$RuCl_3{\cdot}3H_2O/DTPANa_5$	1	1	140	89	99.3	0.7	1060
1/22	$RuCl_3{\cdot}3H_2O/EDTANa_2{\cdot}2H_2O$	1	1	140	86	99.5	0.5	1040
1/23	$RuCl_3{\cdot}3H_2O$/3,4-PyDCA	2	1	140	85	99.0	1.0	1020
1/24	$RuCl_3{\cdot}3H_2O$/BCDS	1	1	140	84	97.4	2.6	1000
1/25	$RuCl_3{\cdot}3H_2O$/NTPA	2	1	140	82	99.4	0.6	980
1/26	$RuCl_3{\cdot}3H_2O/NTANa_3$	2	1	140	82	99.3	0.7	980
1/27	$RuCl_3{\cdot}3H_2O$/EDTA	1	1	140	81	99.5	0.5	970
1/28	$RuCl_3{\cdot}3H_2O$/BSPD	1	1	140	81	99.3	0.7	970
1/29	$RuCl_3{\cdot}3H_2O$/Salen	1	1	140	79	99.5	0.5	950
1/30	$RuCl_3{\cdot}3H_2O$/DTPPA	1	1	140	79	99.1	0.9	950
1/31	$RuCl_3{\cdot}3H_2O$/SANa	2	1	140	78	99.4	0.6	940
1/32	$RuCl_3{\cdot}3H_2O$/TSTPP	1	1	140	75	99.3	0.7	900
1/33	$RuCl_3{\cdot}3H_2O$/TPPTS	2	1	140	71	99.6	0.4	850
1/34	$RuCl_3{\cdot}3H_2O$/BPyDCA	1	1	140	55	100	–	660
1/35	$RuCl_3{\cdot}3H_2O$/PTA	2	1	140	50	100	–	600
1/36	$RuCl_3{\cdot}3H_2O$/DPhPyP	2	1	140	40	99.7	0.3	475

[a] Reaction conditions: P_{H2} = 40 bar; 1.31 mg (0.005 mmol) $RuCl_3{\cdot}3H_2O$; 0.696 g (6 mmol) LA (molar ratio of LA/Ru = 1200); 20 ml of deairated demineralised water; pH = 2.70–3.87; [Ru] = 24 ppm; minor amount of a black precipitate presumed to be metallic ruthenium.
[b] Defined as mole of GVL and mole of formed 1,4-PDO per mole of ruthenium per hour.
[c] 2.62 mg (0.01 mmol) $RuCl_3{\cdot}3H_2O$; 0.871 g (7.5 mmol) LA (molar ratio of LA/Ru = 750); [Ru] = 48 ppm.
[d] No metallic ruthenium formation.

Table 2
Effect of ruthenium catalyst precursor, molar ratio of C = O units/Ru, dihydrogen pressure and the addition of aqueous solvent on the ruthenium-catalyzed hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) in completely aqueous medium[a].

Entry	Catalyst precursor	LA/Ru molar ratio	PH2 (bar)	Water (ml)	Conversion LA (mol %)	Selectivity GVL 1,4-PDO (mol %) (mol %)		TOF[b] (h^{-1})
2/1	$RuCl_3{\cdot}3H_2O$/Taurine	2000	40	20	100	99.9	0.1	2000
2/2[c]	$Ru(NO)(OAc)_3$/Taurine	2000	40	20	100	99.8	0.2	2000
2/3[c]	$Ru(NO)(NO_3)_3$/Taurine	2000	40	20	81	100	–	1620
2/4	$Ru(acac)_3$/Taurine	2000	40	20	72	100	–	1440
2/5[d]	$[Ru(NO)]_2(SO_4)_3$/Taurine	2000	40	20	45	99.5	0.5	890
2/6[c]	$RuO_2{\cdot}H_2O$/Taurine	2000	40	20	38	99.2	0.8	770
2/7	$RuCl_3{\cdot}3H_2O$/Taurine	1200	40	20	98.5	98.8	1.2	1170
2/8	$RuCl_3{\cdot}3H_2O$/Taurine	1600	40	20	92	98.7	1.3	1470
2/9	$RuCl_3{\cdot}3H_2O$/Taurine	2500	40	20	53	99.8	0.2	1330
2/10	$RuCl_3{\cdot}3H_2O$/Taurine	3000	40	20	35	98	2	1060
2/11	$RuCl_3{\cdot}3H_2O$/Taurine	3500	40	20	17	97.6	2.4	580
2/12	$RuCl_3{\cdot}3H_2O$/Taurine	4000	40	20	8	97.4	2.6	310
2/13	$RuCl_3{\cdot}3H_2O$/Taurine	2500	60	20	83	97.3	2.7	2060
2/14	$RuCl_3{\cdot}3H_2O$/Taurine	2500	20	20	10	99.9	0.1	240
2/15	$RuCl_3{\cdot}3H_2O$/Taurine	3000	60	40	58.5	100	–	1755
2/16	$RuCl_3{\cdot}3H_2O$/Taurine	3000	60	20	63	100	–	1880
2/17[c]	$RuCl_3{\cdot}3H_2O$/Taurine	3000	60	10	85	98.4	1.6	2560

[a] Reaction conditions: T = 140 °C; t = 1 h; 0.005 mmol ruthenium catalyst precursor; 1.25 mg (0.01 mmol) taurine (molar ratio taurine/Ru = 2); pH = 2.70–3.65; minor amount of a black precipitate presumed to be metallic ruthenium.
[b] Defined as mole of GVL and mole of formed 1,4-PDO per mole of ruthenium per hour.
[c] Black precipitate presumed to be metallic ruthenium.
[d] Addition of 1.37 mg (0.0025 mmol) $[Ru(NO)]_2(SO_4)_3$ i.e. 0.005 mmol ruthenium; 1.25 mg (0.01 mmol) taurine (molar ratio taurine/Ru = 2).

Table 3
Effect of the addition of various salts, amphiphilic compounds, acids and of the pH value on the ruthenium-catalyzed hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) in completely aqueous medium[a].

Entry	Catalyst precursor	Salts	Salt/Ru molar ratio	pH value	Conversion LA (mol %)	Selectivity GVL 1,4-PDO VA (mol %) (mol %) (mol %)			TOF[b] (h^{-1})
3/1	$RuCl_3{\cdot}H_2O$/Taurine	–	–	2.70	85	98.4	1.6	–	2560
3/2[c]	$RuCl_3{\cdot}H_2O$/Taurine	NaI	100	2.36	1	66.6	16.7	16.7	18
3/3[c]	$RuCl_3{\cdot}H_2O$/Taurine	NaCl	100	2.22	1	92.3	7.7	–	39
3/4	$RuCl_3{\cdot}H_2O$/Taurine	$BaCl_2{\cdot}2H_2O$	50	2.27	8	97.6	1.2	1.2	250
3/5[c]	$RuCl_3{\cdot}H_2O$/Taurine	$AlCl_3{\cdot}6H_2O$	17	2.27	12	98.4	0.8	0.8	360
3/6	$RuCl_3{\cdot}H_2O$ /Taurine	$(CH_3CH_2)_4NBF_4$	100	3.29	7	97.3	1.3	1.3	220
3/7	$RuCl_3{\cdot}H_2O$/Taurine	$NaH_2PO_4{\cdot}H_2O$	100	2.90	16.5	98.8	0.6	0.6	495
3/8[d]	$RuCl_3{\cdot}H_2O$/Taurine	$NaH_2PO_4{\cdot}H_2O$	100	7.00	17	100	–	–	510
3/9[d]	$RuCl_3{\cdot}H_2O$/Taurine	–	–	10.63	23	100		–	680

[a] Reaction conditions: T = 140 °C; P_{H2} = 60 bar; t = 1 h; 1.31 mg (0.005 mmol) $RuCl_3{\cdot}3H_2O$; 1.25 mg (0.01 mmol) taurine (molar ratio taurine/Ru = 2); 1.741 g (15 mmol) LA (molar ratio LA/Ru = 3000); 10 ml of deairated demineralised water; [Ru] = 24 ppm; black precipitate presumed to be metallic ruthenium.
[b] Defined as mole of GVL and mole of formed 1,4-PDO and VA per mole of ruthenium per hour.
[c] No metallic ruthenium formation.
[d] pH was adjusted with 5% aqueous NaOH.

Table 4
Effect of the molar ratio of C = O units/Ru at a low amount of aqueous solvent of 10 and 5 ml on the catalytic activity and recycling experiments of the Ru/BPhDS catalyst in the hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) in completely aqueous medium[a].

Entry	Catalyst precursor	LA/Ru molar ratio	Water (ml)	Conversion LA (mol %)	Selectivity GVL 1,4-PDO (mol %) (mol %)		TOF[b] (h^{-1})
4/1	$RuCl_3{\cdot}3H_2O$/BPhDS	3300	10	57	99.2	0.8	1880
4/2	$RuCl_3{\cdot}3H_2O$/BPhDS	3300	5	70	99.7	0.3	2300
4/3	$RuCl_3{\cdot}3H_2O$/BPhDS	3000	5	100	99.9	0.1	3000
4/4	$RuCl_3{\cdot}3H_2O$/BPhDS	2400	10	100	98.4	1.6	2400
4/5[c]	Recycled catalyst	2400	10	98	99.1	0.9	2370

[a] Reaction conditions: T = 140 °C; P_{H2} = 80 bar; t = 1 h; 1.31 mg (0.005 mmol) $RuCl_3{\cdot}3H_2O$; 2.86 mg (0.005 mmol) BPhDS (molar ratio BPhDS/Ru = 1); pH = 2.43–2.86; [Ru] = 42–75 ppm; No metallic ruthenium formation.
[b] Defined as mole of GVL and mole of formed 1,4-PDO per mole of ruthenium per hour.
[c] The aqueous catalyst layer (10 ml) of entry 4/4, after extraction with diethyl ether and separation of the upper organic phase, was re-used with addition of a new portion of 1.393 g (12 mmol C = O units) of LA.

aqueous reaction mixture having a pH value of 2.43 was removed. The product mixture was analyzed by gas chromatography (GC) after addition of N,*N*-dimethylformamide as standard and the obtained results are given in entry 4/3 of Table 4. Emphasis has been placed in all reaction described in Tables 1–4 in order to obtain reproducible results.

2.3. Analyses

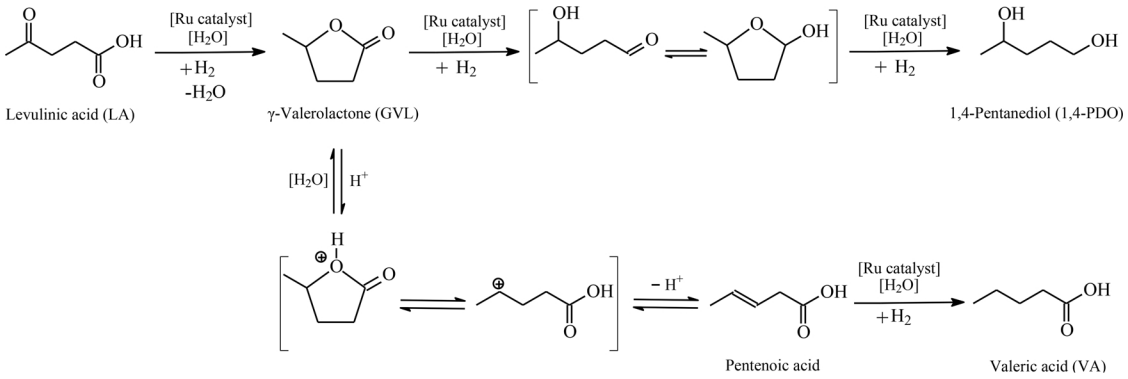
The purity of the TPPTS ligand was determined by quantitative $^{31}P\{^1H\}$NMR analysis in D_2O at 25 °C. δ TPPTS = -5.4 ppm. $^{31}P\{^1H\}$NMR spectra (121 MHz, referenced to external 85% H_3PO_4) were recordered on a Varian Unity Plus 300/54 spectrometer. The hydrogenation product γ-valerolactone (GVL) and the side products 1,4-pentanediol (1,4-PDO) and valeric acid (VA)were identified by comparison of GC and gas chromatography/mass spectrometry (GC/MS) analytic data with data for authentic samples. GC/MS was measured on an Agilent 6890 N GC coupled with an Agilent 5975B MS. The GC was equipped with a HP-5MS column (30 m x 0.25 mm i.d. x 0.25 µm film thickness). Carrier gas was He with 2 ml/min. Injector system: pulsed splitless. The injector and detector temperatures were set at 300 °C and 250 °C, respectively. Ms quad: 150 °C, MS source: 230 °C. The oven temperature was initially at 60 °C for 0 min and then increased to 240 °C with a rate of 10 °C/min. The GC analyses were run on a Shimadzu GC-14B equipped with a FID detector and a HP-Innowax capillary column (30 m x 0.251 mm i.d. x 0.50 µm film thickness) which was purchased from Agilent Technologies. Carrier gas was N_2 at 100 kPa. The oven temperature was initially at 120 °C for 0 min and then increased to 240 °C at 10 °C/min. The injector and detector temperatures both were set at 240 °C.

3. Results and discussion

3.1. Selective hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) catalyzed by water-soluble ruthenium systems modified with nitrogen-containing ligands in aqueous media

Ruthenium based catalysts are the systems of the choice for the hydrogenation of LA which contains 2 reactive functional groups (−C═O and $-CO_2H$) because of the inherent ability of ruthenium to hydrogenate selectively a carbonyl moiety into an alcohol group to form the intermediate 4-hydroxyvaleric acid which subsequently readily undergoes dehydration to yield by highly favorable intramolecular esterification the C_5 cyclic ester product namely GVL (Scheme 1). Due to the high oxygen content and, therefore, the hydrophilicity of levulinic acid the hydrogenation on its C═O group should be carried out in aqueous media. Furthermore, it is well known in the literature [42,35,47,87] that the presence of water as a solvent has a beneficial effect in LA hydrogenation reactions catalyzed by heterogeneous and nanoparticles ruthenium based catalytic systems. LA hydrogenation reactions catalyzed by heterogeneous ruthenium catalysts in THF and water together with DFT calculations in a joint experimental and theoretical study have shown that the presence of H-bonded water molecules dramatically reduces the energetic span of the reaction pathway thus enhancing the catalytic activity in the aqueous medium [42]. Addition of water accelerated the rates in Ru/C-catalyzed hydrogenation reactions of LA to GVL [35]. Similarly, the highest conversions in the LA hydrogenations to GVL were obtained in water while in organic solvents significantly lower yields were observed using ruthenium nanoparticle catalysts [47,87].

We chose water-soluble nitrogen-containing ligands to modify



Scheme 2. Catalytic hydrogenation of LA beyond GLV to produce 1,4-pentanediol (1,4-PDO) and valeric acid (VA).

ruthenium catalysts and applied in the LA hydrogenation reaction in aqueous media because of the superior activity of palladium catalysts modified with nitrogen-containing ligands compared with TPPTS in the hydrogenation reaction of renewable polyunsaturated methyl esters of soybean oil to their monounsaturated counterparts in aqueous/organic two-phase micellar systems [105]. Moreover, we chose water-soluble nitrogen-containing ligands such as BPhDS, taurine etc. to modify ruthenium catalysts for the hydrogenation of LA to GVL because such catalytic systems are not susceptible to air oxygen and palladium catalysts modified with nitrogen-containing ligands such as BPhDS and taurine have been applied even in aerobic oxidation reactions of terminal olefins to methyl ketones in aqueous media [106,107]. We have studied the influence of operating reaction parameters such as the ligand/ruthenium molar ratio, reaction time, temperature, nature of ligands, nature of ruthenium catalyst precursors, the molar ratio of LA/Ru, hydrogen pressure, added aqueous solvent, salts, amphiphilic compounds, acids and of the pH value on the hydrogenation reaction of LA in order to achieve high catalytic activities and selectivities to GVL and performed recycling experiments to prove the stability of the water-soluble ruthenium catalyst modified with nitrogen-containing ligands in aqueous media.

3.1.1. Effect of the ligand/ruthenium molar ratio

First, we investigated the influence of the L/Ru molar ratio on the hydrogenation of LA catalyzed by water-soluble $RuCl_3{\cdot}3H_2O$ catalysts precursors modified with the nitrogen-containing ligand bathophenanthrolinedisulfonic acid disodium salt (BPhDS, Fig. 1) at a ruthenium concentration of 48 ppm in water in the absence of any added organic solvent within 1 h of reaction time (Table 1, entries 1/1-1/3). As expected, the highest catalytic activity with a turnover frequency (TOF) of 390 h^{-1} was obtained at a low BPhDS/Ru molar ratio of 1 (entry 1/1) whereas at increasing ligand/metal molar ratios the catalytic activity decreases to give at a ratio of BPhDS/Ru = 3 a TOF value of 230 h^{-1} (entry 1/3). This lower catalytic activity at higher BPhDS/Ru molar ratios could probably be rationalized by assuming that a competition between the free BPhDS ligand and the C=O units of LA for a coordination site on ruthenium takes place which may lead to a retardation in the activation of the LA hydrogenation reaction. Similarly, the group of Joó [102] also observed a retarding effect of excess of water-soluble TPPMS ligand added to ruthenium precursor in Ru/TPPMS-catalyzed hydrogenation reactions in aqueous media. Furthermore, the group of Sheldon [106,107] has shown in Pd/BPhDS-catalyzed aerobic oxidation reactions of terminal olefins to methyl ketones in aqueous media that the best results were also obtained at a BPhDS/Pd molar ratio of 1. The Ru/BPhDS-catalyzed hydrogenation reaction of LA is highly selective to give at the low L/Ru molar ratios of 1 and 2 quantitative selectivities towards GVL (Table 1, entries 1/1 and 1/2) and at the higher molar ratio of L/Ru = 3 the selectivity to GVL remained high (99.6 mol%) with a formation of 0.4 mol% of the side product 1,4-pentanediol (1,4-PDO) (entry 1/3). After the hydrogenation reaction no metallic ruthenium formation was observed at the BPhDS/Ru molar ratio of 3 (entry 1/3) indicating no decomposition of the catalyst whereas at the lower molar ratios BPhDS/Ru = 2 and 1 a minor amount of metallic ruthenium was formed indicating to a minor extent decomposition of the catalyst (entries 1/2, 1/1).

3.1.2. Effect of reaction time and temperature

Next, the effect of reaction time was investigated on the activity and selectivity of the water-soluble Ru/BPhDS catalysts in the hydrogenation reaction of LA in aqueous media (Table 1, entries 1/1 and 1/4-1/6). The conversion of LA increases with increasing reaction time from 1 up to 6 h to give values from 52 up to 100 mol% with very high selectivities to GVL from 99.5 to 100 mol% in aqueous media (Table 1, entries 1/1, 1/4-1/6). Even at a longer reaction time of 6 h the selectivity of GVL remained high (99.6 mol%) with a small formation of the side product 1,4-PDO of only 0.4 mol% (entry 1/6) which is obtained from GVL hydrogenation (Scheme 2). The reaction pathway for the formation of 1,4-PDO from GVL hydrogenation has been described by Geilen et al. [66] and involves hydrogenation of the C=O bond of GVL to form the cyclic hemiacetal compound which is in equilibrium with the open 4-hydroxypentanal form followed by further hydrogenation of the carbonyl functional group to yield 1,4-PDO (Scheme 2).

The catalytic activity in the $RuCl_3{\cdot}3H_2O$/BPhDS-catalyzed hydrogenation of LA to GVL increases with increasing temperature from 100 °C up to 160 °C to give TOFs from 120 up to 1200 h^{-1} with conversions of LA from 10 up to 100 mol%, respectively, and high selectivities to GVL from 98.7 up to 99.8 mol% with 1,4-PDO formations of 0.2 up to 1.3 mol% at a molar ratio of LA/Ru = 1200 and a ruthenium concentration of only 24 ppm in the aqueous monophasic system (Table 1, entries 1/7 - 1/13). Using the $RuCl_3{\cdot}3H_2O$/BPhDS catalytic system after the hydrogenation reaction no metallic ruthenium formation was observed at reaction temperatures from 100 up to 140 °C indicating no decomposition of the catalyst (entries 1/7-1/11) whereas at higher temperatures from 150 up to 160 °C a minor amount of metallic ruthenium was formed after the reaction indicating to a minor extent decomposition of the catalyst (entries 1/11-1/13). It should be pointed out that at a reaction temperature of 120 °C under the same reaction conditions with, however, a lower molar ratio of LA/Ru = 750 and a higher ruthenium concentration 48 ppm in the aqueous medium a minor amount of metallic ruthenium was formed after the reaction (Table 1, entry 1/1) probably because of the presence of a lower amount of LA which has a stabilizing effect on the Ru/BPhDS catalyst by coordination with both the −COOH and C=O functionalities in the highly polar aqueous medium. The apparent Arrhenius parameter of the activation energy of the Ru/BPhDS-catalyzed hydrogenation reaction of LA in aqueous media was calculated from results obtained from hydrogenation reactions carried out at temperatures 100–160 °C and are summarized in Table 1, entries 1/7-1/13. The apparent activation energy which was calculated with these data (Fig. 2) amounts to 53.3 kJ/

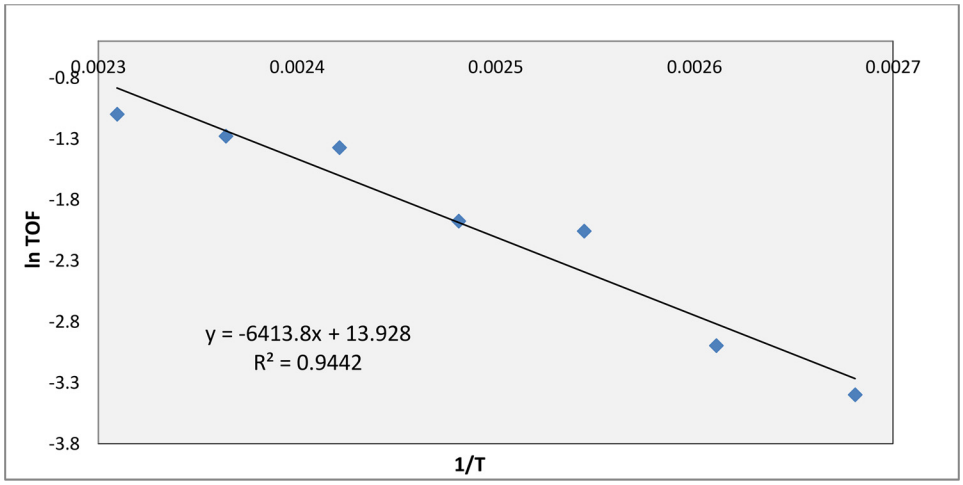


Fig. 2. Calculation of the apparent Arrhenius parameter of the activation energy of the hydrogenation reaction of LA catalyzed by water-soluble Ru/BPhDS catalysts in aqueous media.

mol. The relatively low apparent activation energy of 53.3 kJ/mol indicates for the presence of an active ruthenium catalyst modified with the nitrogen-containing BPhDS ligand to reduce in LA a less reactive keto group into alcohol functionality in the highly polar aqueous medium.

3.1.3. Effect of the ligands on the ruthenium catalyzed hydrogenation of LA

Table 1, entries 1/11 and 1/14-1/36 show the activity and selectivity of in-situ formed water-soluble ruthenium catalytic systems in the hydrogenation of LA as a function of different phosphines and various nitrogen-containing ligands (Fig. 1) in aqueous media. The highest catalytic activity (TOF = 1170 h^{-1}) with a conversion of LA of 98.5 mol% and selectivities towards GVL of 98.8 mol% and 1,4-PDO of 1.2 mol% in the hydrogenation reaction of LA was achieved with $RuCl_3{\cdot}3H_2O$ catalysts precursors modified with water-soluble taurineligands (Fig. 1) at a ruthenium concentration of only 24 ppm in the aqueous phase (Table 1, entry 1/14). In contrast, the catalytic activity exhibited the $RuCl_3{\cdot}3H_2O$ catalyst precursor modified with the TPPTS benchmark ligand (Fig. 1) was much lower (TOF = 850 h^{-1}) with a conversion of LA of 71.0 mol% and selectivity to GVL of 99.6 mol% and to 1,4-PDO of 0.4 mol% under the same conditions in this hydrogenation reaction (Table 1, entry 1/33). However, this activity of 850 TOFs per hour we obtained with $RuCl_3{\cdot}3H_2O$/TPPTS catalysts is much higher compared with the activity of only 210 TOFs per hour in the study of Delhomme et al. [84] using the same catalytic system $RuCl_3{\cdot}3H_2O$/TPPTS at the same reaction temperature of 140 °C even at a higher hydrogen pressure of 55 bar in the hydrogenation reaction of LA to GVL in aqueous media. In the study of Delhomme et al. [84] the water-soluble $RuCl_3{\cdot}3H_2O$/TPPTS catalyst exhibited a selectivity to GVL of 91 mol% and with the water-soluble $Ru(acac)_3$/TPPTS catalyst the activity was 202 TOFs per hour with a selectivity towards GVL of 97 mol% [84] which are lower compared with the selectivity to GVL of 99.6 mol % we obtained with $RuCl_3{\cdot}3H_2O$/TPPTS catalysts (Table 1, entry 1/33). The group of Tukacs [83] applied $Ru(acac)_3$ catalysts modified with a sulfonated phosphine comparable with TPPTS which is nBuP(C_6H_4-*m*-$SO_3Na)_2$ in the hydrogenation of LA in the absence of solvents and found a high catalytic activity of 3540 TOFs per hour under 100 bar hydrogen pressure at 140 °C and a selectivity to GVL of 99.9 mol% which is comparable with the selectivity to GVL of 99.6 mol% we obtained with $RuCl_3{\cdot}3H_2O$/TPPTS catalysts in aqueous media (Table 1, entry 1/33). High catalytic activities (TOF = 1160–1110 h^{-1}) and high selectivities to GVL of 98.6–99.9 mol% were exhibited by $RuCl_3{\cdot}3H_2O$ precursors modified with trans-1,2-diaminocyclohexane-*N,N,*N´,N´-tetraacetic acid (CyDTA, Fig. 1), tris(2-pyridyl)phosphine (T_2PyP), 2,2´-biquinoline-4,4´dicarboxylic acid dipotassium salt (BQC) and 3-pyridinesulfonic acid (3-PSA) ligands in the hydrogenation of LA in the aqueous phase (Table 1, entries 1/15-1/18). The catalytic hydrogenation activity exhibited by $RuCl_3{\cdot}3H_2O$ catalyst precursors modified with the nitrogen containing water-soluble ligands ethylenediaminetetraacetic acid tetrasodium salt (EDTA·Na_4), 2,6-pyridinedicarboxylic acid (2,6-PyDCA), diethylenetriaminepentaacetic acid pentasodium salt (DTPA·Na_5), ethylenediaminetetraacetic acid disodium salt (EDTA·Na_2), 3,4-pyridinedicarboxylic acid (3,4-PyDCA), bathocuproinedisulfonic acid disodium salt (BCDS), nitrilotris(methylphosphonic acid) (NTPA), nitrilotriacetic acid trisodium salt (NTA·Na_3), ethylenediaminetetraacetic acid (EDTA), N,N´-bis(salicylidene)-1,3-propanediamine (BSPD), N,N´-bis(salicylidene)ethylenediamine (Salen), diethylenetriaminepentakis(methylphosphonic acid) (DTPPA), sulfanilic acid sodium salt (SANa), bathophenanthrolinedisulfonic acid disodium salt (BPhDS) and tetrasodium meso-tetra(sulfonatophenyl)porphine (TSTPP) are in the range of 1090 and 900 TOF's per hour and the selectivities to GVL of 97.4–99.6 mol% (Table 1, entries 1/11 and 1/19 - 1/32) which are still higher than the catalytic activity (TOF = 850 h^{-1}) exhibited by $RuCl_3{\cdot}3H_2O$/TPPTS catalyst (Table 1, entry 1/33). Using the water-soluble ligands 2,2´-bipyridine-4,4´-dicarboxylic acid (BPyDCA), 1,3,5-triaza-7-phosphaadamantane (PTA) and diphenyl(2-pyridyl)phosphine (DPhPyP) as modifiers of $RuCl_3{\cdot}3H_2O$ precursors the catalytic LA hydrogenation activities obtained were lower from 660 down to 475 TOF's per hour (Table 1, entries 1/34 - 1/36). In general, in the aqueous-phase hydrogenation reaction of LA the catalytic activities exhibited $RuCl_3{\cdot}3H_2O$ precursors modified with water-soluble phosphines such as TPPTS and PTA were lower with 850 and 600 TOFs per hour, respectively (Table 1, entries 1/33 and 1/35) compared with the activities exhibited with nitrogen-containing ligands such as taurine, BQC and 3-PSA with 1170, 1120 and 1110 TOFs per hour, respectively (entries 1/17 and 1/18) or with P^N chelating ligands such as T_2PyP to achieve 1160 TOFs per hour (entry 1/16). In order to explain the higher catalytic activities exhibited water-soluble ruthenium catalysts modified with nitrogen-containing ligands compared with their ruthenium phosphine counterparts in the aqueous-phase hydrogenation reaction of LA to GVL we consider the mechanistic study by Geilen et al. [65] for this reaction catalyzed by $[Ru(TriPhos)H]^+$ in ionic liquids. In this reaction mechanism [65] hydride transfer from the Ru-H group to the carbon atom of coordinated C═O group of LA takes place followed by protonation of the resulting Ru-O group via σ-bond metathesis from a nonclassical coordinated dihydrogen molecule, η^2-H_2, regenerating at the same time the catalytically active classical hydride, Ru-H, group. The heterolytic cleavage of the nonclassical coordinated dihydrogen molecule and the associated protonation of the Ru-O group may be assisted by basic centers which may reduce the

energy barrier for both the cleavage and protonation steps even further [65]. According to this mechanism [65] we assume that in the aqueous-phase ruthenium-catalyzed hydrogenation of LA in the presence of nitrogen-containing compounds which act both as ligands to ruthenium and as bases their N-atoms facilitates both steps the heterolytic cleavage of coordinated dihydrogen molecule and the associated protonation of the Ru-O group to obtain GVL with higher reaction rates compared with ruthenium catalysts modified with phosphines because phosphines are weaker bases compared with their nitrogen-containing counterparts. Moreover, the high catalytic activities exhibited ruthenium catalysts modified with water-soluble ligands in the aqueous-phase hydrogenation of LA, in general, were rationalized by assuming that the nature of the highly polar aqueous medium also facilitates both steps the heterolytic cleavage of coordinated dihydrogen molecule and the associated protonation of the Ru-O group to obtain GVL as described in the above mentioned reaction mechanism [65]. It should also be mentioned that using N-ligands containing electron-donating substituents the catalytic activity increased in the ruthenium-catalyzed aqueous-phase hydrogenation reaction of LA which is in accordance with the effect described in the literature [85] by pentamethylcyclopentadienyliridium catalysts modified with N-ligands where the catalytic activity also increased considerably with ligands containing electron-donating substituents such as 4,4´-dihydroxy-2,2´-bipyridine in the LA hydrogenation reaction in aqueous media. For example, using $RuCl_3{\cdot}3H_2O$ catalyst precursors modified with BCDS ligands (Fig. 1) containing two electron-donating methyl groups in the α-positions to both nitrogen atoms the catalytic activity was higher (TOF = 1000 h^{-1}, entry 1/24) compared with the activity (TOF = 910 h^{-1}, entry 1/11) exhibited $RuCl_3{\cdot}3H_2O$ catalysts modified with BPhDS ligands (Fig. 1) which have not such electron-donating methyl groups. Similarly, using CyDTA ligands (Fig. 1) containing the electron-donating cyclohexane group to the nitrogen atoms to modify $RuCl_3{\cdot}3H_2O$ precursors the catalytic activity was higher (1160 TOFs per hour, entry 1/15) compared with the activity (970, 1040 and 1090 TOFs per hour, entries 1/27, 1/22, 1/19) exhibited the same catalyst precursor modified with EDTA,EDTA·Na_2 and EDTA·Na_4 ligands (Fig. 1) which have not such electron-donating groups.

3.1.4. Effect of ruthenium catalyst precursor and of molar ratio LA/Ru

In the hydrogenation reaction of LA in the presence of water-soluble ruthenium complexes with taurine ligands the catalytic activity of ruthenium precursors decreased in the order: $RuCl_3{\cdot}3H_2O \approx Ru(NO)(OAc)_3 > Ru(NO)(NO_3)_3 > Ru(acac)_3 > [Ru(NO)]_2(SO_4)_3 > RuO_2{\cdot}H_2O$ to give TOF's of 2000 h^{-1}, 1620 h^{-1}, 1440 h^{-1}, 890 h^{-1} and 770 h^{-1}, respectively in aqueous media (Table 2, entries 2/1-2/6). Using $RuCl_3{\cdot}3H_2O$, $Ru(acac)_3$ and $[Ru(NO)]_2(SO_4)_3$ catalyst precursors modified with taurine ligands after the hydrogenation reaction a minor amount of metallic ruthenium was observed indicating to a minor extent decomposition of the catalyst whereas with $Ru(NO)(OAc)_3$, $Ru(NO)(NO_3)_3$ and $RuO_2{\cdot}H_2O$ precursors modified with taurine ligands after the reaction more metallic ruthenium was formed indicating decomposition of the catalyst.

The LA/Ru molar ratio has a pronounced effect on the activity and selectivity in the $RuCl_3{\cdot}3H_2O$/taurine-catalyzed hydrogenation reaction of LA in aqueous media. The catalytic activity increased from TOF = 1170 h^{-1} to TOF = 1470 h^{-1} while the selectivity to GVL remains almost unchanged high (98.8–98.7 mol%) with increasing molar ratios of LA/Ru from 1200 to 1600 in the hydrogenation of LA in aqueous media (Table 2, entries 2/7 and 2/8). Raising the LA/Ru molar ratio higher has a negative effect on the reaction rate and on the selectivity to GVL in the aqueous-phase hydrogenation of LA. Thus, the catalytic activity decreased from TOF = 1330 h^{-1} down to TOF = 310 h^{-1} and the selectivity to GVL decreased from 99.8 to 97.4 mol% whereas the selectivity towards 1.4-PDO increased from 0.2 to 2.6 mol% with increasing LA/Ru molar ratios from 2500 up to 4000 (entries 2/9 - 2/12).

3.1.5. Effect of hydrogen pressure and of added aqueous solvent

The hydrogen pressure has a pronounced effect on the activity in the hydrogenation of LA and is shown in entries 2/9, 2/13 and 2/14 of Table 2. The catalytic activity increased from TOF = 240 h^{-1} to TOF = 2060 h^{-1} and the selectivity towards GVL decreased from 99.9 mol% down to 97.3 mol% with increasing hydrogen partial pressure from 20 to 60 bar at a ruthenium concentration of only 24 ppm in the aqueous monophasic system. At the low hydrogen pressure of 20 bar the selectivity to 1,4-PDO was 0.1 mol% and with increasing pressure the selectivity to 1,4-PDO increased to give under 60 bar H_2 2.7 mol% of 1,4-PDO.

The $RuCl_3{\cdot}3H_2O$/taurine-catalyzed hydrogenation reaction of LA was carried out at different mount of added aqueous solvent in the range of 40 to 10 ml within 1 h of reaction time. The catalytic activity increased from 1755 up to 2560 TOFs per hour with decreasing amount of added water as a solvent from 40 down to 10 ml (Table 2, entries 2/15 - 2/17). The selectivity to GVL decrease with decreasing amount of added aqueous solvent i.e. with 40 ml water the selectivity to GVL was 100.0 mol% whereas with 10 ml water the selectivity drops to 98.4 mol % with 1.6 mol% formation of the 1,4-PDO byproduct. The effect of higher catalytic activity at lower amount of added water could probably be explained with the higher concentration of ruthenium which was 43 ppm in the presence of 10 ml of added aqueous solvent whereas the concentration of ruthenium was only 12 ppm in the presence of 40 ml of added water as solvent. It should also be mentioned that in the presence of 40 and 20 ml of added water after the hydrogenation reaction a minor amount of metallic ruthenium was observed indicating to a minor extent decomposition of the catalyst (entries 2/15 and 2/16) whereas with 10 ml of added aqueous solvent after the reaction more metallic ruthenium was formed indicating decomposition of the Ru/taurine catalyst (entry 2/17).

3.1.6. Effect of salts, amphiphilic compounds, acids and of the pH value

Addition of various salts with strongly coordinating anions such as NaI, NaCl and $BaCl_2{\cdot}2H_2O$ have a detrimental effect on the catalytic activity of the $RuCl_3{\cdot}3H_2O$/taurinesystem to obtain TOF values from 18 up to 250 per hour (Table 3, entries 3/2 - 3/4) compared with the high activity of TOF = 2560 h^{-1} exhibited by the $RuCl_3{\cdot}3H_2O$/taurine catalyst in the absence of salts (entry 3/1) in the hydrogenation reaction of LA at a reaction temperature of 140 °C under 60 bar of hydrogen pressure and molar ratios of LA/Ru = 3000 and taurine/Ru = 2, addition of 10 ml of deairated demineralized water with a ruthenium concentration of only 24 ppm at pH values from 2.22 up to 2.70 within 1 h of reaction time. Interestingly, in the $RuCl_3{\cdot}3H_2O$/taurine-catalyzed hydrogenation reaction of LA in the presence of the strongly coordinating NaI the selectivity to GVL drops to 66.6 mol% with a higher formation of 16.7 mol% of 1,4-PDO and of 16.7 mol% of valeric acid (VA) (entry 3/2). According to the mechanism proposed by the group of Dumesic [37,103] protonation of GVL leads to ring-opening of GVL through intermedites bearing carbenium ions to produce pentenoic acid which is subsequently hydrogenated to yield VA (Scheme 2). The remarkable selectivity exhibited $RuCl_3{\cdot}3H_2O$/taurine/NaI systems in acidic aqueous medium in the hydrogenation of LA to GVL and subsequent GVL hydrogenation to produce 1,4-PDO and VA could probably be explained by the formation of catalytic active ruthenium species with coordinated iodide ligands. Such Ru/taurine/I catalytic key intermediates may be active in the ring-opening hydrogenation of GVL to yield 1,4-PDO (Scheme 2) and also capable after protonation to the ring-opening of GVL [37,103] with stabilization of formed intermediates bearing a carbenium ion at the γ-carbon atom by I- moieties to facilitate the formation of pentenoic acid [37,103] which is further hydrogenated to VA (Scheme 2). Furthermore, in the presence of NaI after the hydrogenation reaction no metallic ruthenium was observed indicating no decomposition of the catalyst (entry 3/2). Addition of Lewis acids such as $AlCl_3{\cdot}6H_2O$ and of amphiphilic compounds with non-coordinating counter anions such as $(CH_3CH_2)_4N^+BF_4^-$ the

catalytic activity of the $RuCl_3{\cdot}3H_2O$/taurinesystem remained low to give 360 and 220 TOFs per hour, respectively with high selectivities to GVL from 98.4 to 97.3 mol% (entries 3/5, 3/6).

The hydrogenation of LA catalyzed by $RuCl_3{\cdot}3H_2O$/taurine systems is influenced by the pH value of the aqueous phase (Table 3, entries 3/1, 3/7 - 3/9). The highest catalytic activity (TOF = 2560 h^{-1}) was achieved under acidic conditions at pH 2.70 in the absence of any added buffer (entry 3/1) whereas with addition of $NaH_2PO_4{\cdot}H_2O$ at pH 2.90 the activity drops to 495 TOFs per hour (entry 3/7). This high decrease in catalytic activity from 2560 to 495 TOF's per hour could probably be explained with the increased ionic strength of the solution due to the presence of added $NaH_2PO_4{\cdot}H_2O$ salt at a molar ratio of salt/Ru = 100. It is well known in the field of aqueous-phase catalysis that addition of different salts as a means to increase the solution ionic strength gives rise to a dramatic drop in catalytic activity of e.g. water-soluble Rh/TPPTS catalysts in aqueous-phase hydroformylation reaction of olefins [104], water-soluble Pd/TPPTS catalysts in aqueous-phase carbonylations reactions of HMF [88–90] and of 1-(4-isobutylphenyl)ethanol to yield ibuprofen [108,109] and of water-soluble Ru/TPPTS, Rh/TPPTS and Pt/TPPTS catalysts in aqueous-phase hydrogenation reactions of polyunsaturated methyl esters of vegetable oils into their monounsaturated counterparts [110–115]. The hydrogenation reaction of LA catalyzed by $RuCl_3{\cdot}3H_2O$/taurine systems with addition of $NaH_2PO_4{\cdot}H_2O$ salt under acidic conditions at pH 2.90 (entry 3/7) was carried out in order to be able to study the effect of pH value under similar conditions because for the adjustment of pH 7.00 it is necessary to add the $NaH_2PO_4{\cdot}H_2O$ salt to create the NaH_2PO_4/NaOH-buffer. The catalytic activity was slightly higher under neutral conditions at pH 7.00 adjusted by a NaH_2PO_4/NaOH-buffer (TOF = 510 h^{-1}, entry 3/8) and slightly increased under basic conditions at pH 10.63 to give a TOF of 680 h^{-1} (entry 3/9).

3.1.7. Effect of the LA/Ru molar ratio at low amounts of water and recycling experiments

The $RuCl_3{\cdot}3H_2O$/BPhDS catalytic system is stable at the reaction temperature of 140 °C and therefore was selected to investigate the influence of the reaction parameter of C = O units/Ru molar ratio on the selective hydrogenation of LA at low amounts of 10 and 5 ml added aqueous solvent (Table 4, entries 4/1 - 4/3). In the $RuCl_3{\cdot}3H_2O$/BPhDS-catalyzed hydrogenation of LA at 140 °C under 80 bar of hydrogen and molar ratios of LA/Ru = 3300 and BPhDS/Ru = 1 at low mounts of added aqueous solvent in the range of 10 down to 5 ml with ruthenium concentrations of 42 and 73 ppm, respectively, under acidic conditions with pH values from 2.48 to 2.45 within 1 h of reaction time the catalytic activity increased from 1880 up to 2300 TOFs per hour with increasing conversions of LA from 57 to 70 mol% upon decreasing amounts of added water from 10 down to 5 ml (entries 4/1 and 4/2). Under the same reaction conditions using $RuCl_3{\cdot}3H_2O$/BPhDS catalysts at a lower molar ratio of LA/Ru = 3000 with addition of 5 ml of aqueous solvent by a ruthenium concentration of 75 ppm and pH value of 2.43 the conversion of LA was quantitative and the catalytic activity further increased to achieve a TOF value of 3000 h^{-1} with essentially quantitative selectivity to GVL of 99.9 mol% and formation of only 0.1 mol % of the 1,4-PDO byproduct (entry 4/3). Using $RuCl_3{\cdot}3H_2O$/BPhDS catalytic systems at 10 and 5 ml added aqueous solvent after the hydrogenation reactions (entries 4/1 - 4/3) no metallic ruthenium formation was observed indicating no decomposition of the catalyst.

A recycling experiment with a consecutive run were carried out in the hydrogenation of LA in order to get more information for the stability of Ru/BPhDS catalysts in the aqueous medium (Table 4, entries 4/4 and 4/5). 1.31 mg (0.005 mmol) $RuCl_3{\cdot}3H_2O$ and 2.86 mg (0.005 mmol) BPhDS (molar ratio BPhDS/Ru = 1) were dissolved under argon in 10 ml of deairated demineralized H_2O and the mixture was stirred for about 5 min at room temperature to give a clear, red coloured, solution. After addition of 1.393 g (12 mmol) LA to the aqueous catalyst solution under stirring for further 5 min the aqueous reaction mixture, having a ruthenium concentration of 44 ppm, was charged into an *Autoclave Engineers* autoclave of a nominal volume of 100 ml which was previously evacuated and filled with argon. In the reaction mixture the molar ratio of LA/Ru was 2400. After a number of pressurizing-depressurizing cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured and contents were heated with stirring using a stir bar driven by an IKA magnetic stirrer (poorer mixing) because its own MagneDrive III agitator system was out of order (stirring rate = 700 rpm). The heating time to reach a reaction temperature of 140 °C was 5 min. At the reaction temperature of 140 °C the hydrogen partial pressure was 80 bar and the reaction time 1 h. After the reaction the autoclave was cooled (within 3 min) to room temperature, vented of hydrogen and the aqueous reaction mixture was removed. A sample of 120 mg was taken from the aqueous reaction mixture and was analyzed by gas chromatography (GC) after addition of N,*N*-dimethylformamide as standard (entry 4/4). Subsequently, 10 ml of diethyl ether were added to the 10 ml of the aqueous reaction mixture to create a biphasic system. The Ru/BPhDS catalyst was easily recovered from reaction products by intensive extraction using a separatory funnel being shaken very well by hands for 5 min and a simple phase separation of the lower aqueous red coloured layer from the upper organic product uncoloured layer. The lower aqueous layer containing the Ru/BPhDS catalyst after addition of a new portion of 1.393 g (12 mmol) of LA (molar ratio of LA/Ru = 2400) was re-used under the same hydrogenation reaction conditions. After the recycling hydrogenation experiment no metallic ruthenium formation was observed indicating a stable catalyst and the pH value of the aqueous catalyst solution was 2.86. The catalytic activity remained high (TOF = 2370 h^{-1}) using the recycled Ru/BPhDS catalyst in the aqueous-phase hydrogenation experiment of entry 4/5 compared with the first hydrogenation reaction of LA of entry 4/4 catalyzed by the same Ru/BPhDS system (TOF = 2400 h^{-1}). These results have shown that the ruthenium catalyst modified with the nitrogen-containing bidentate ligand BPhDS is stable without loss of activity and selectivity which is remarkable when one considers that reaction parameters such as the temperature of 140 °C and the acidic aqueous medium (pH = 2.86) are rather demanding conditions for a homogeneous catalytic hydrogenation reaction.

It is relevant to point out, that after the hydrogenation reaction it is necessary to add low amounts such as 10 ml of diethyl ether to 10 ml of the aqueous catalytic reaction mixture to create a biphasic system in order to extract the reaction products in the upper organic layer from the lower aqueous catalyst layer for the recovery and recycling of the Ru/BPhDS catalyst. If higher amounts such as 20 ml of diethyl ether were added for the extraction of 10 ml aqueous reaction mixture the catalytic activity dramatically decreases in the consecutive LA hydrogenation run mainly due to the diethyl ether and to a lesser extent of the GVL and 1,4-PDO products [LA was not present because of the quantitative conversion in the first run (entry 4/4)] which are inevitably dissolved in small amounts in the highly polar aqueous catalyst solution which gives rise to a drop in the polarity of the LA hydrogenation reaction mixture which effect is in accordance with literature data [42,35,47,87] that the presence of the aqueous medium accelerates the rates in ruthenium-catalyzed hydrogenation reactions of LA to GVL whereas in organic solvents significantly lower yields were observed using such catalysts in the LA hydrogenation reaction.

4. Conclusions

We have shown that in the presence of water-soluble ruthenium catalysts modified with various nitrogen-containing ligands the hydrogenation of levulinic acid (LA) into γ-valerolactone (GVL) proceeds smoothly with high catalytic activities up to 3000 TOFs per hour and essentially quantitative selectivity to GVL of 99.9 mol% with a formation of only 0.1 mol % of the 1,4-pentanediol (1,4-PDO) byproduct using $RuCl_3{\cdot}3H_2O$ catalysts precursors modified with e.g. the

bathophenanthrolinedisulfonic acid disodium salt ligand (BPhDS) in aqueous media.

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